# Fluctuation and Stress Relaxation Dynamics in a Block Copolymer Melt

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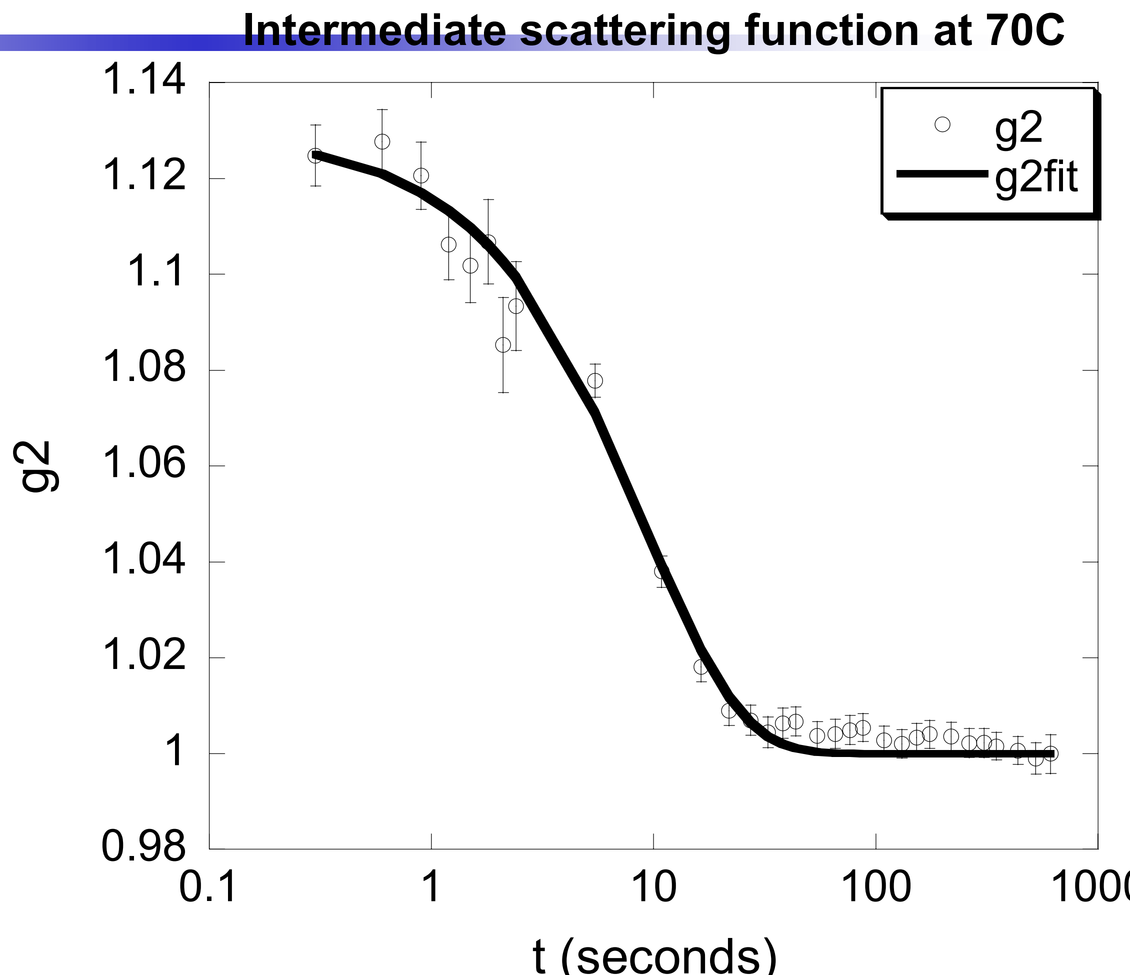
# X-ray photon correlation spectroscopy (XPCS)

- Is a powerful tool for probing the dynamics of concentration fluctuations in diblock copolymers.
- Measures an intensity autocorrelation function which is usually a decaying function.



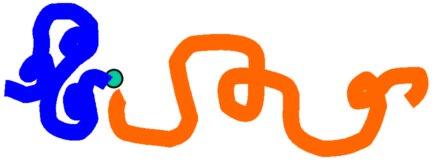

$$g2(t) \equiv \frac{< I(q^*,0) I(q^*,t) >}{< I(q^*,t) >^2} = 1 + k e^{-2t/\tau_{XPCS}}$$

$\tau_{XPCS}$=XCPS relaxation time

$k$=contrast factor

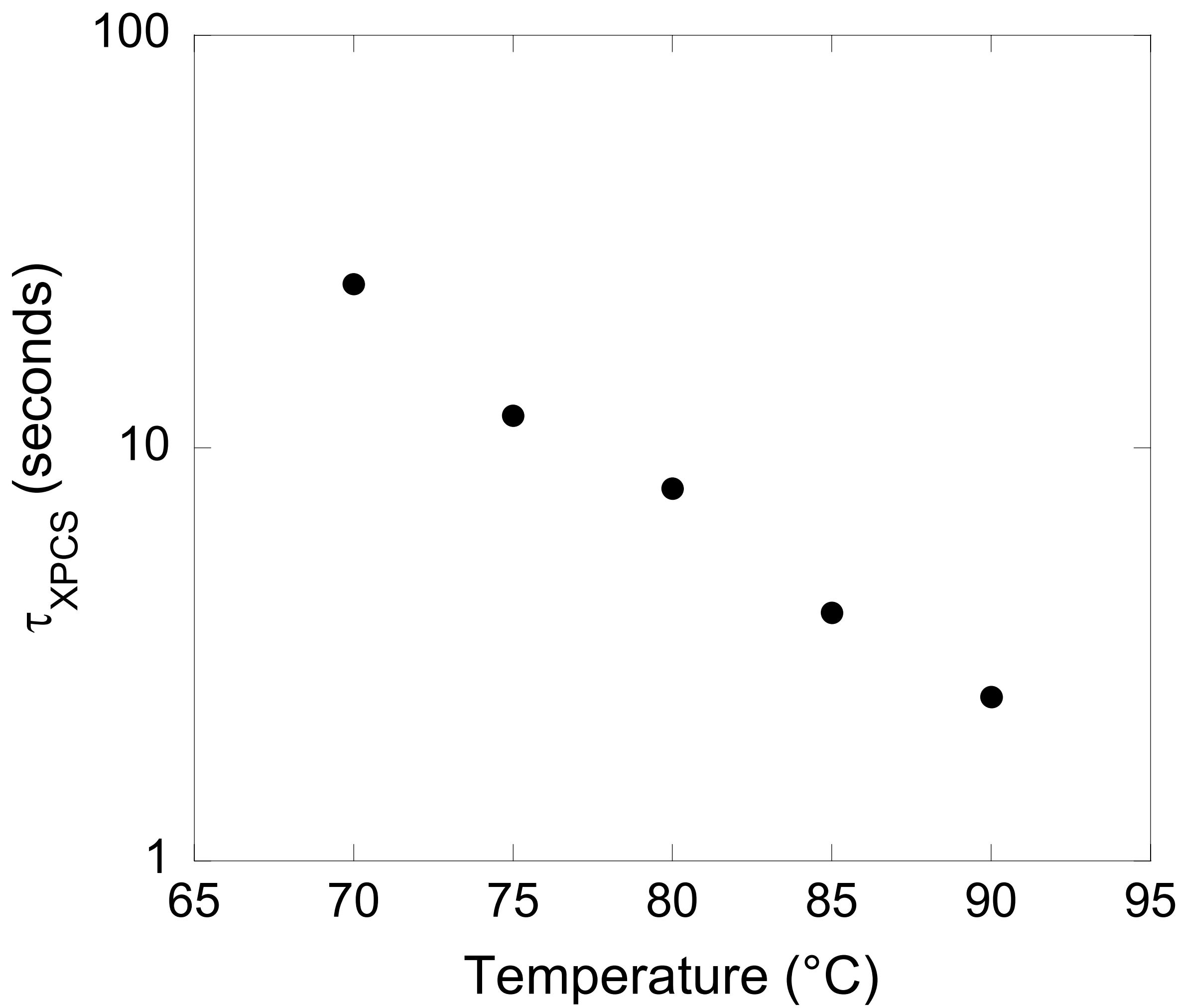
# Characterization

- Poly(Styrene-*block*-isoprene) (SI)



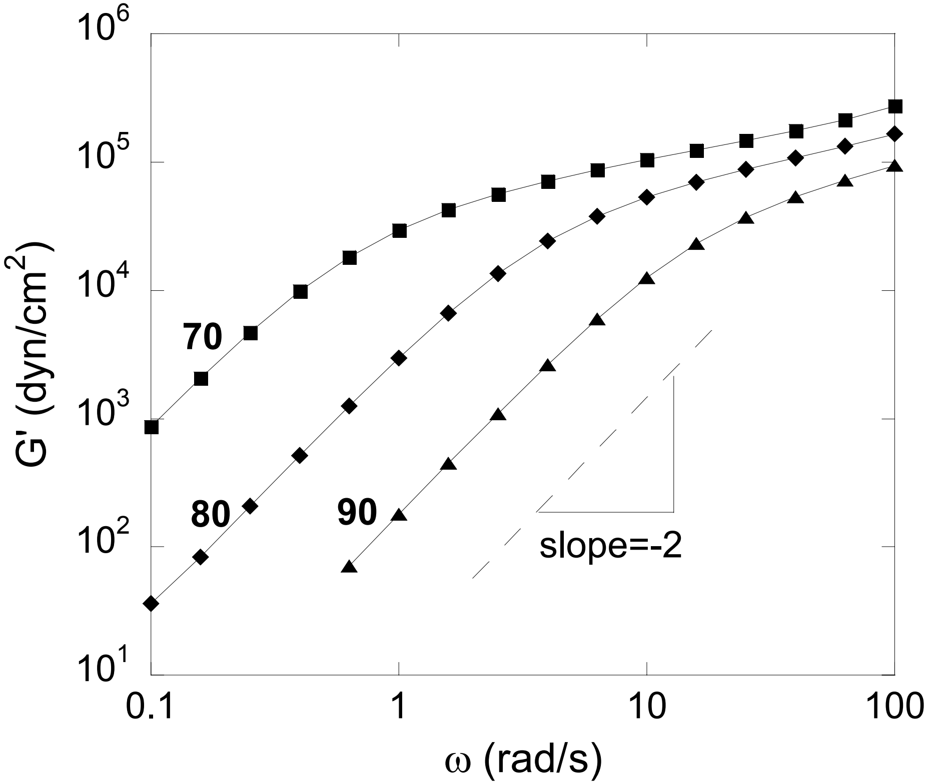
- Mol. Wt. =33,000g/mol
- Vol. Fraction of styrene=0.18
- Order-to-disorder transition at 70°C from hexagonally packed cylinders to disordered micelles(locally stable concentration fluctuations).

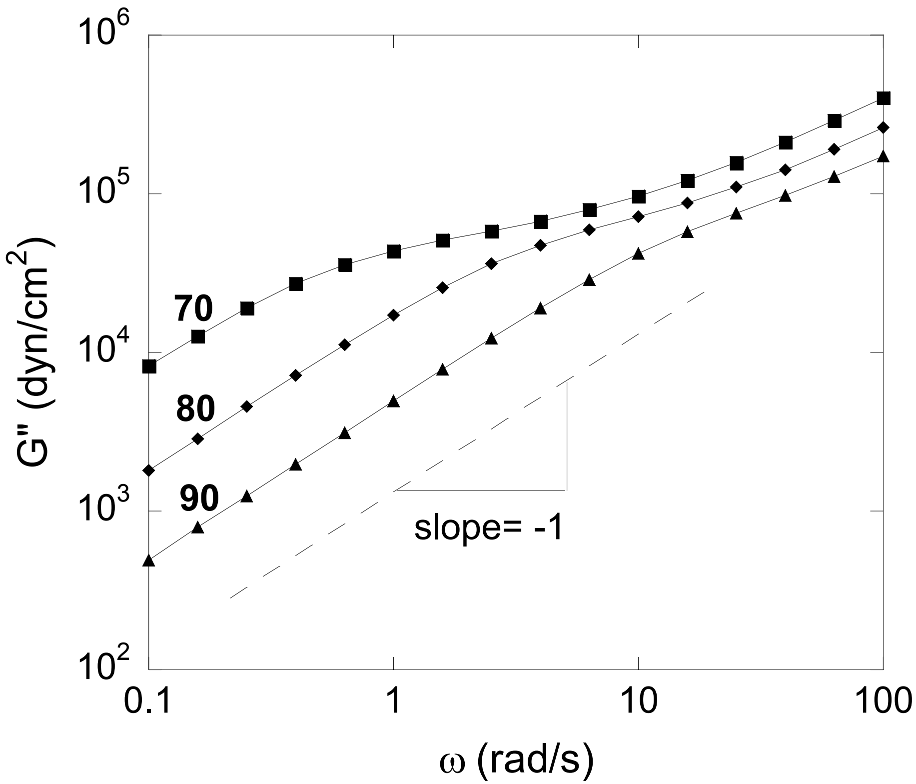
# XPCS relaxation times for SI



# Rheology on SI

- The storage (G’) and loss (G”) moduli show terminal (liquid-like) behavior in the temperature range (70-90°C) where micelles are present. i.e. G’~$\omega^{-2}$ and G”~ $\omega^{-1}$



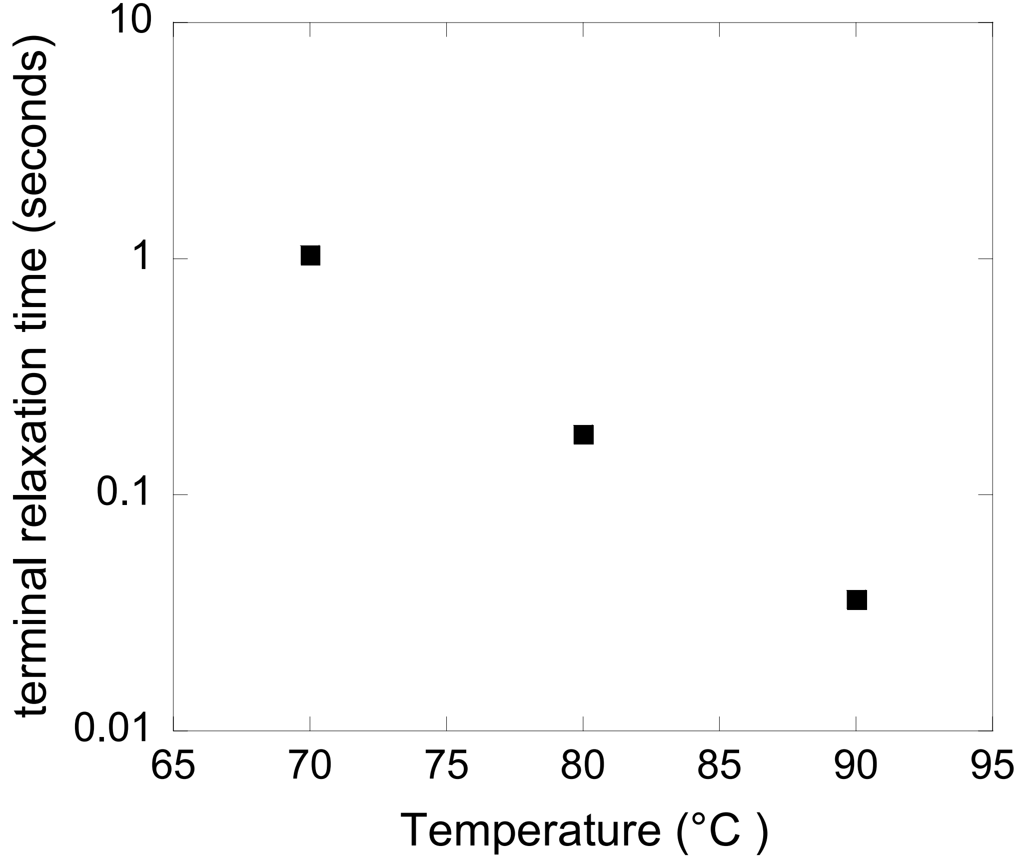
# Terminal relaxation times

- From the low frequency rheology data, we can compute the terminal relaxation time, which is the so-called longest relaxation time for the relaxation of the diblock copolymer chains.

$\tau_{rheo} = J_e \eta_0$

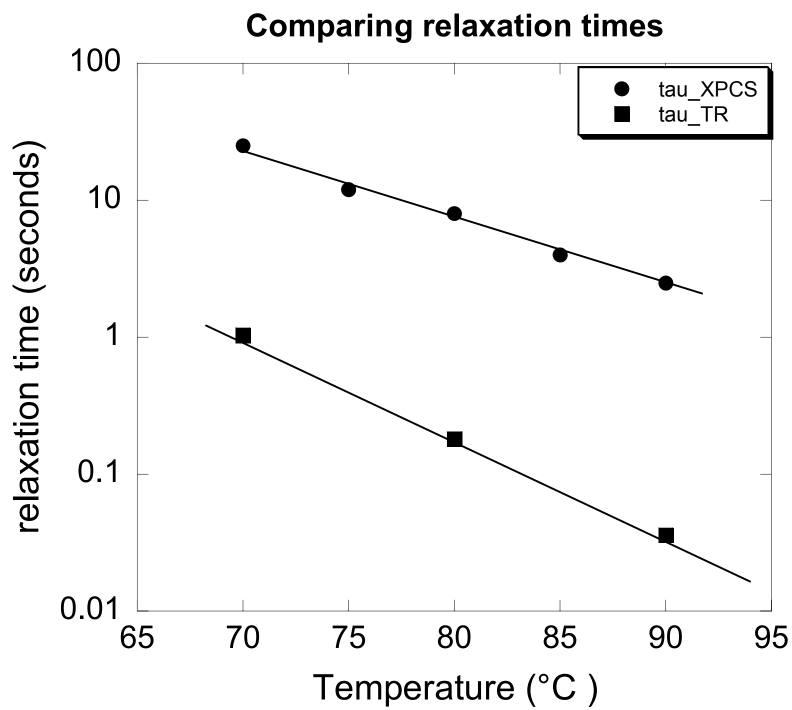
$J_e = [G'(\omega)/\{G''(\omega)\}^2]$ as $\omega \rightarrow 0$

$\eta_0 = [G''(\omega)/\ \omega]$ as $\omega \rightarrow 0$



# $\tau_{XPCS}$ Vs $\tau_{TR}$

- $\tau_{XPCS}$, the microscopic relaxation time is 1-2 orders of magnitude larger than $\tau_{TR}$, the so-called longest relaxation time!
- Also, the temperature dependencies of $\tau_{XPCS}$ and $\tau_{TR}$ are similar but not identical.



# Fredrickson Larson Theory

$$G'(\omega) = \frac{k_B T \omega^2}{30\pi^2 R_g^3} \int_0^{x_c} x^{5/2} \frac{S^2(x)}{\omega^2 + 4\overline{\omega}^2(x)} \left[ \frac{\partial S^{-1}(x)}{\partial x} \right] dx$$

$$G''(\omega) = \frac{k_B T \omega}{15\pi^2 R_g^3} \int_0^{x_c} x^{5/2} \frac{S^2(x)\overline{\omega}(x)}{\omega^2 + 4\overline{\omega}^2(x)} \left[ \frac{\partial S^{-1}(x)}{\partial x} \right] dx$$

$$\overline{\omega}(x) = \tfrac{1}{2\tau} x g(x) N S^{-1}(x)$$

$$\tau_{\mathrm{rheo}} = J_e \eta_0$$

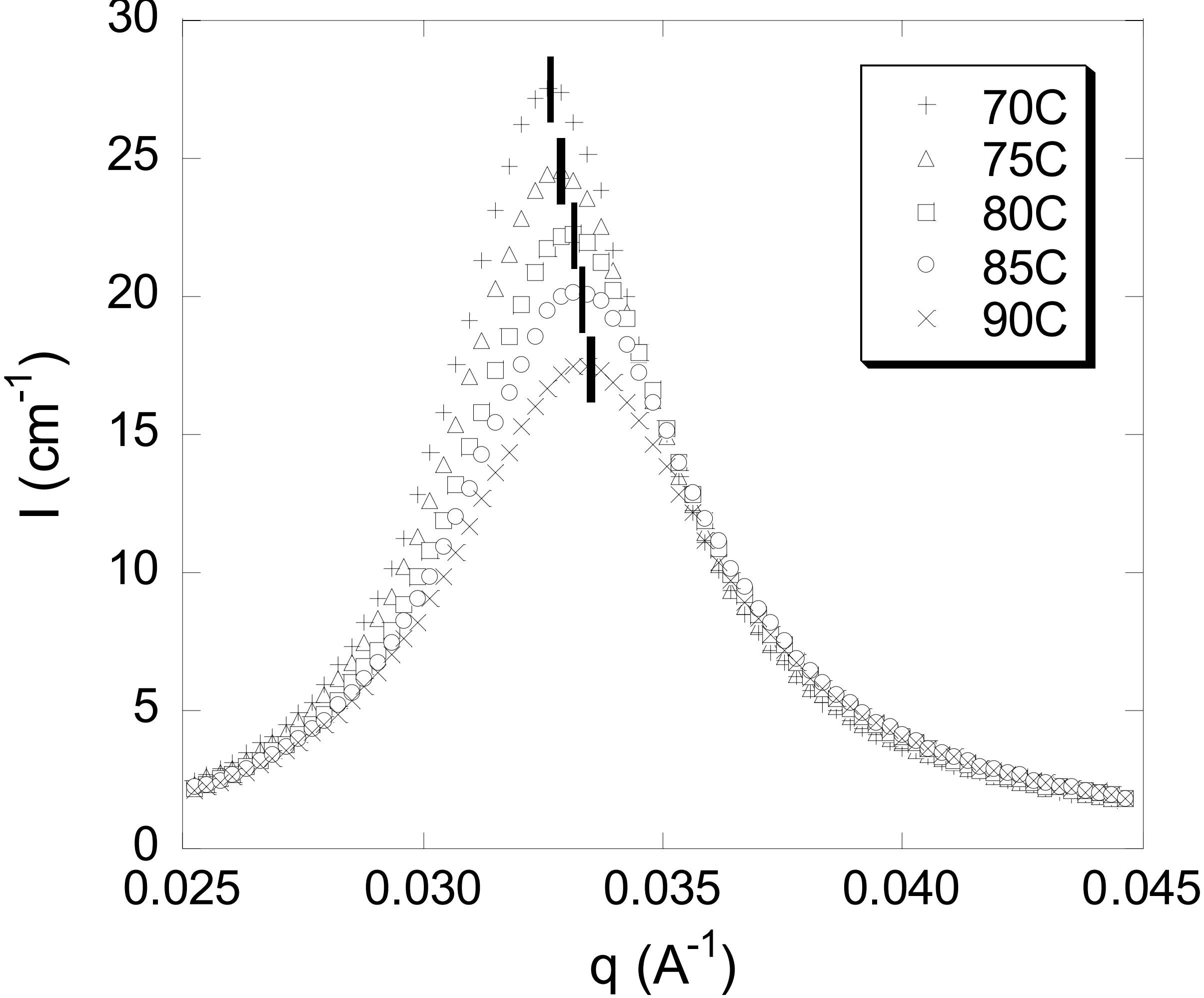
$$\tau_{XPCS} = 1/\overline{\omega}(x^*)$$

$$J_e = [G'(\omega)/\{G''(\omega)\}^2] \text{ as } \omega \to 0$$

$$\eta_0 = [G''(\omega)/\omega] \text{ as } \omega \to 0$$

$$\frac{\partial}{\partial t} P[\psi, t] = \int \frac{d\vec{k}}{(2\pi)^3} \frac{\delta}{\delta\psi(\vec{k})} \left\{ k^2 \lambda(k) \left[ \frac{\delta}{\delta\psi(-\vec{k})} + \beta \frac{\delta H[\psi]}{\delta\psi(-\vec{k})} \right] - \dot{\gamma}(t) k_x \frac{\partial}{\partial k_y} \psi(\vec{k}) \right\} P[\psi, t]$$

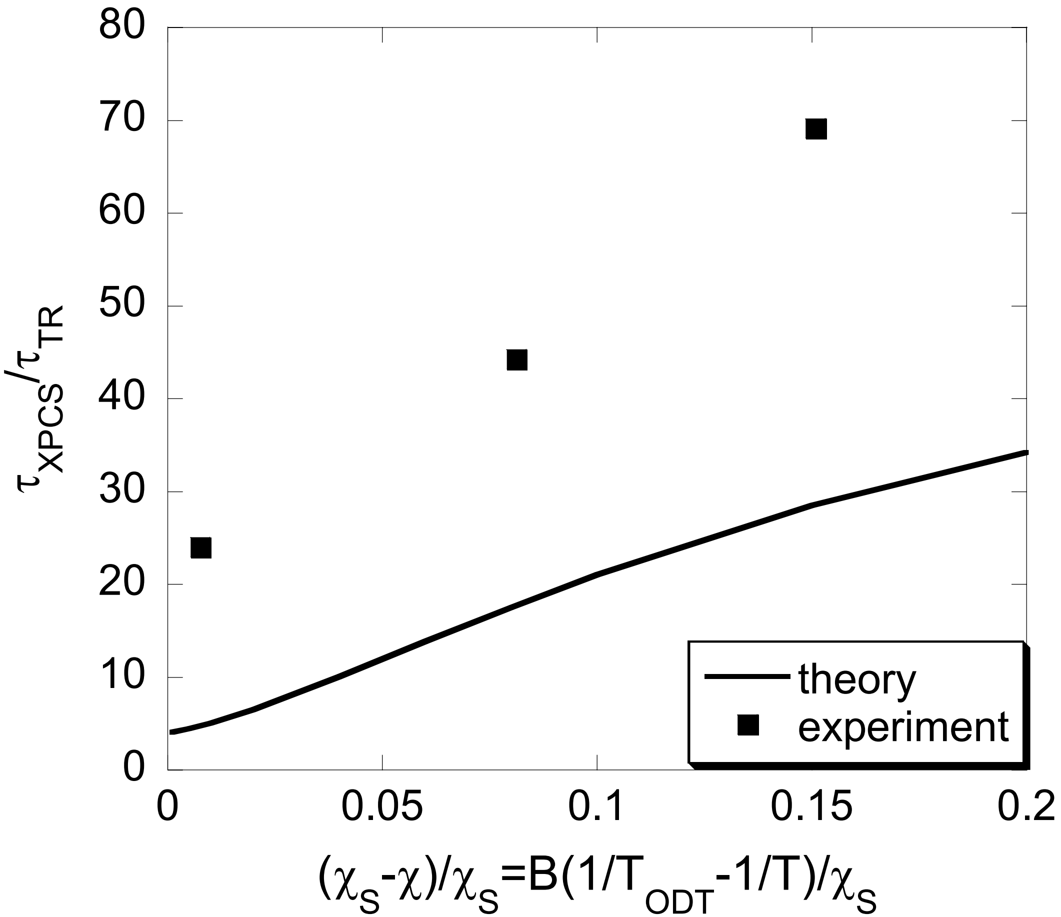
# S(q) as a function of temperature




Fredrickson and Larson quantified of "de Gennes narrowing"

# Comparing theory and experiment

- The fact that $\tau_{XPCS}/\tau_{TR}$ is greater than 1 is in agreement with theory
- Near the ODT, $\tau_{XPCS}/\tau_{TR}$ is an increasing function of the distance from the transition.
- The experimentally meaured $\tau_{XPCS}/\tau_{TR}$ is greater than the theoretical prediction.

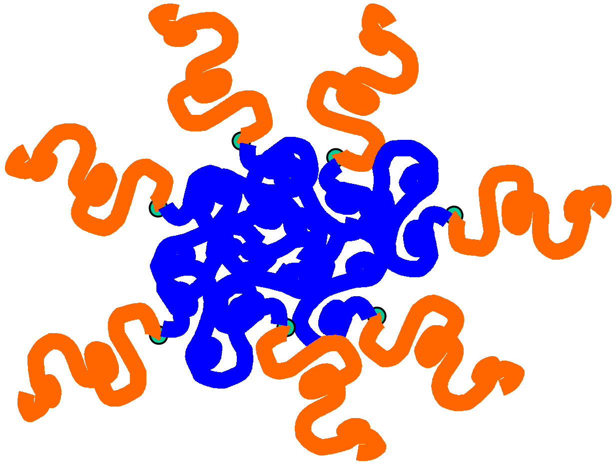


# Dynamics of SI using XPCS

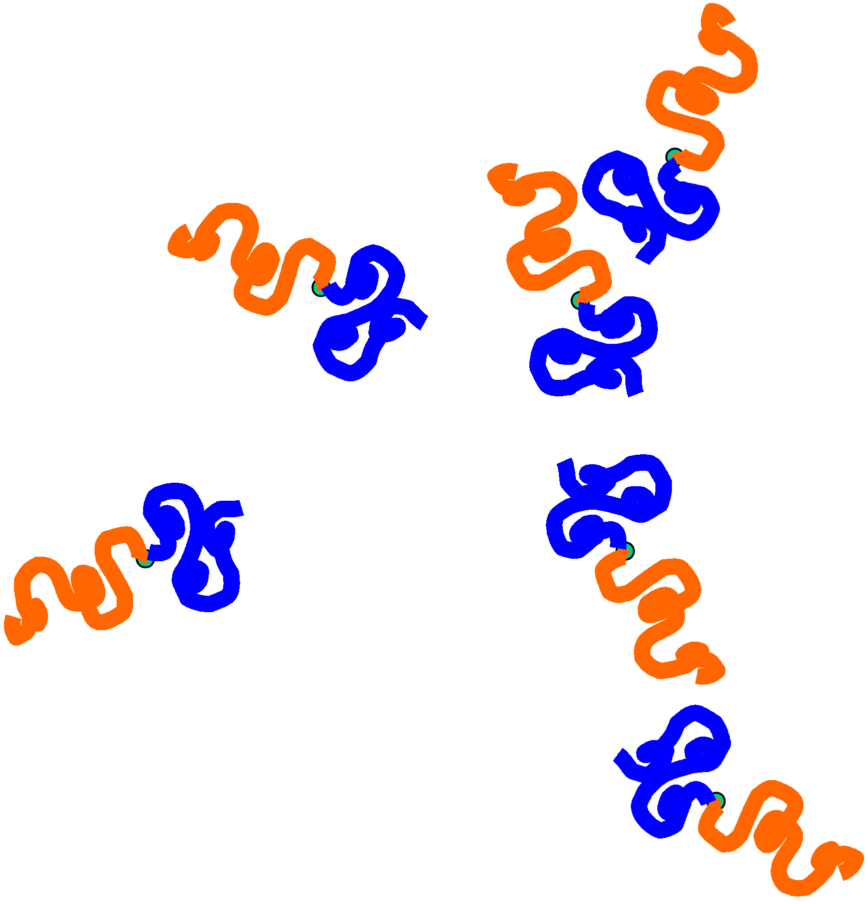
- The time constant $\tau$, measured by XPCS could be postulated to arise from one of the following two processes:

1. Diffusion of the micelles.
2. Dissolution of the micelles.

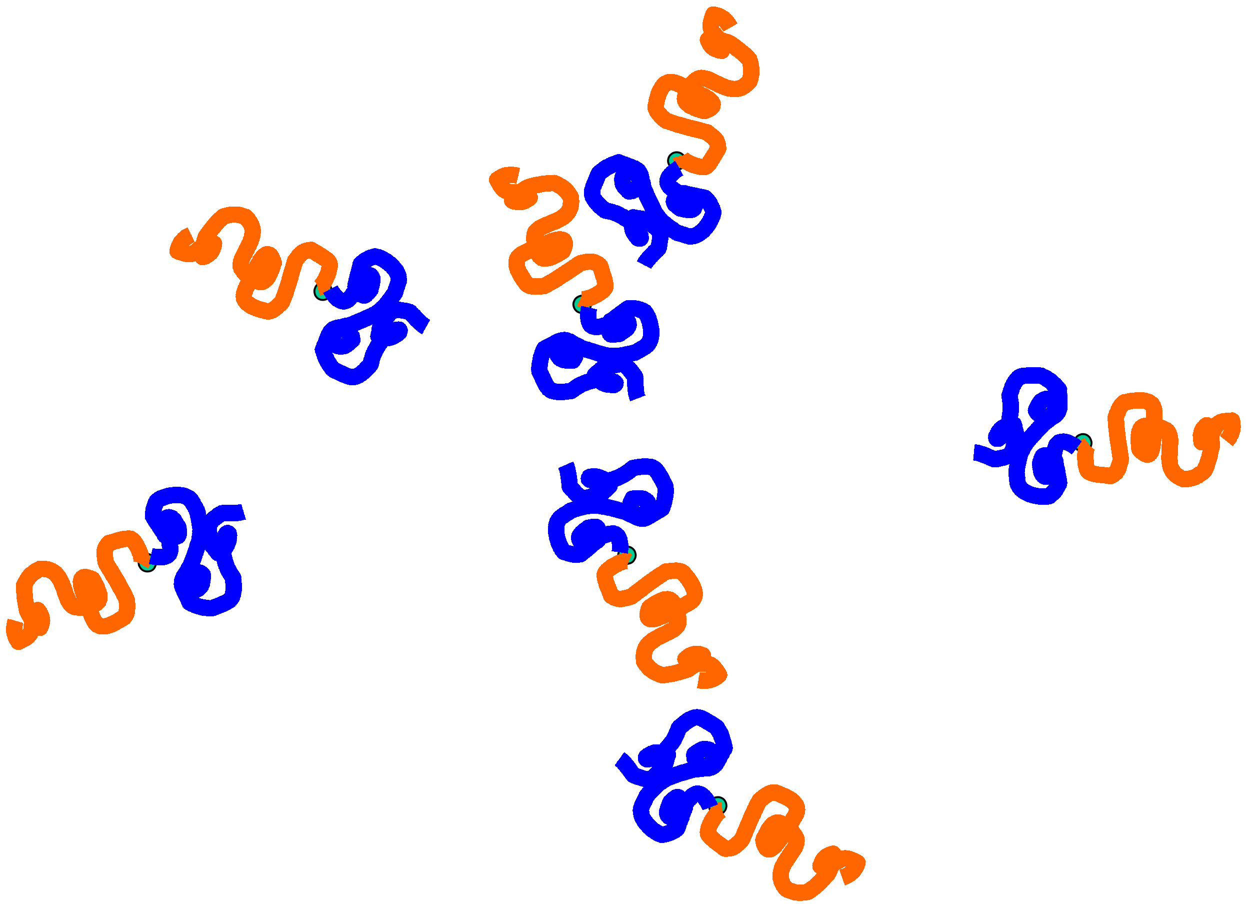
# Micelles fall apart and reassemble



# Micelles fall apart and reassemble $\tau_{diss}$



# Micelles fall apart and reassemble $\tau_{diss}$



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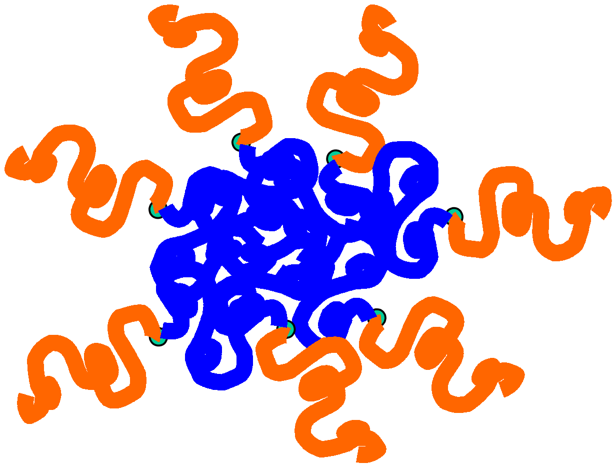
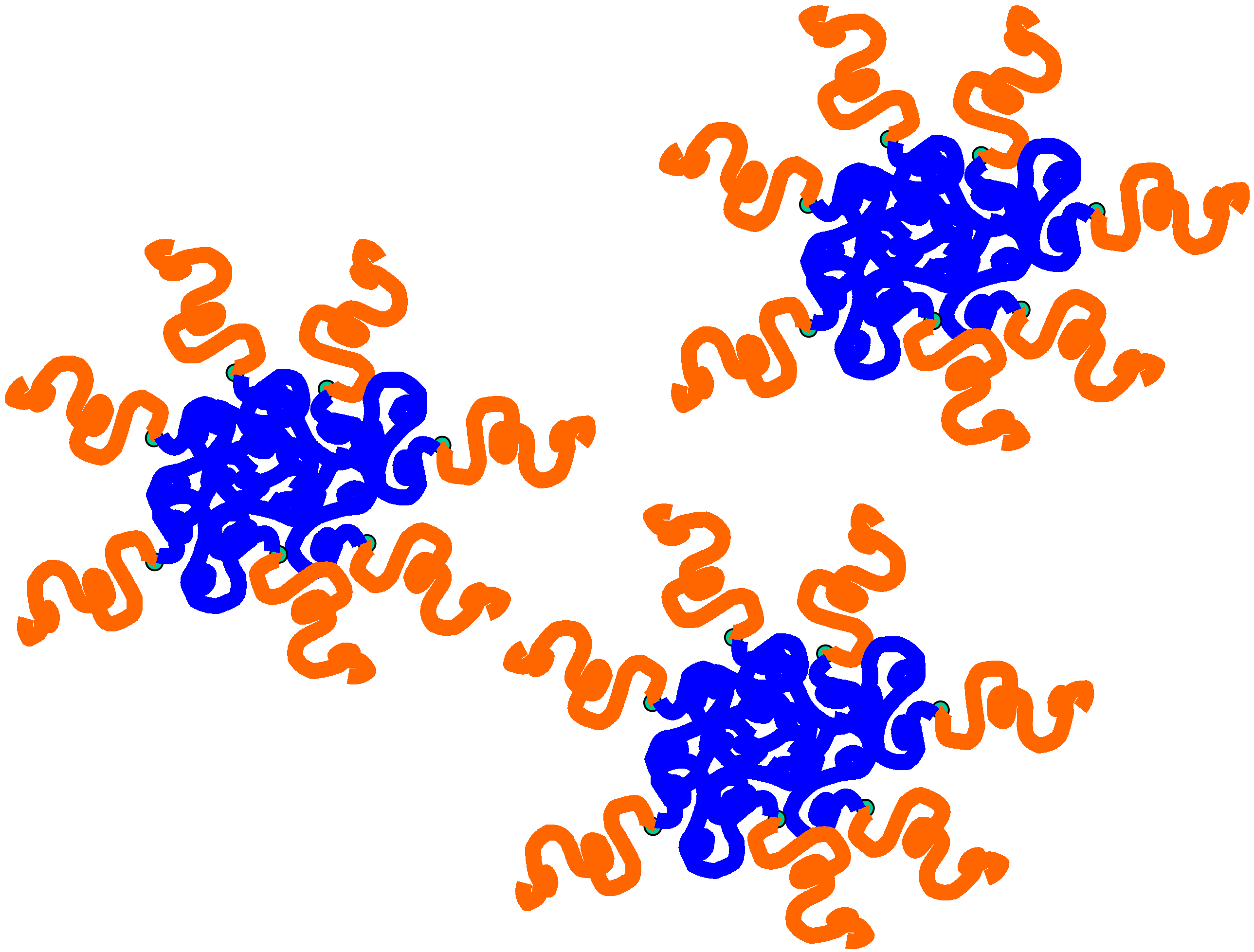
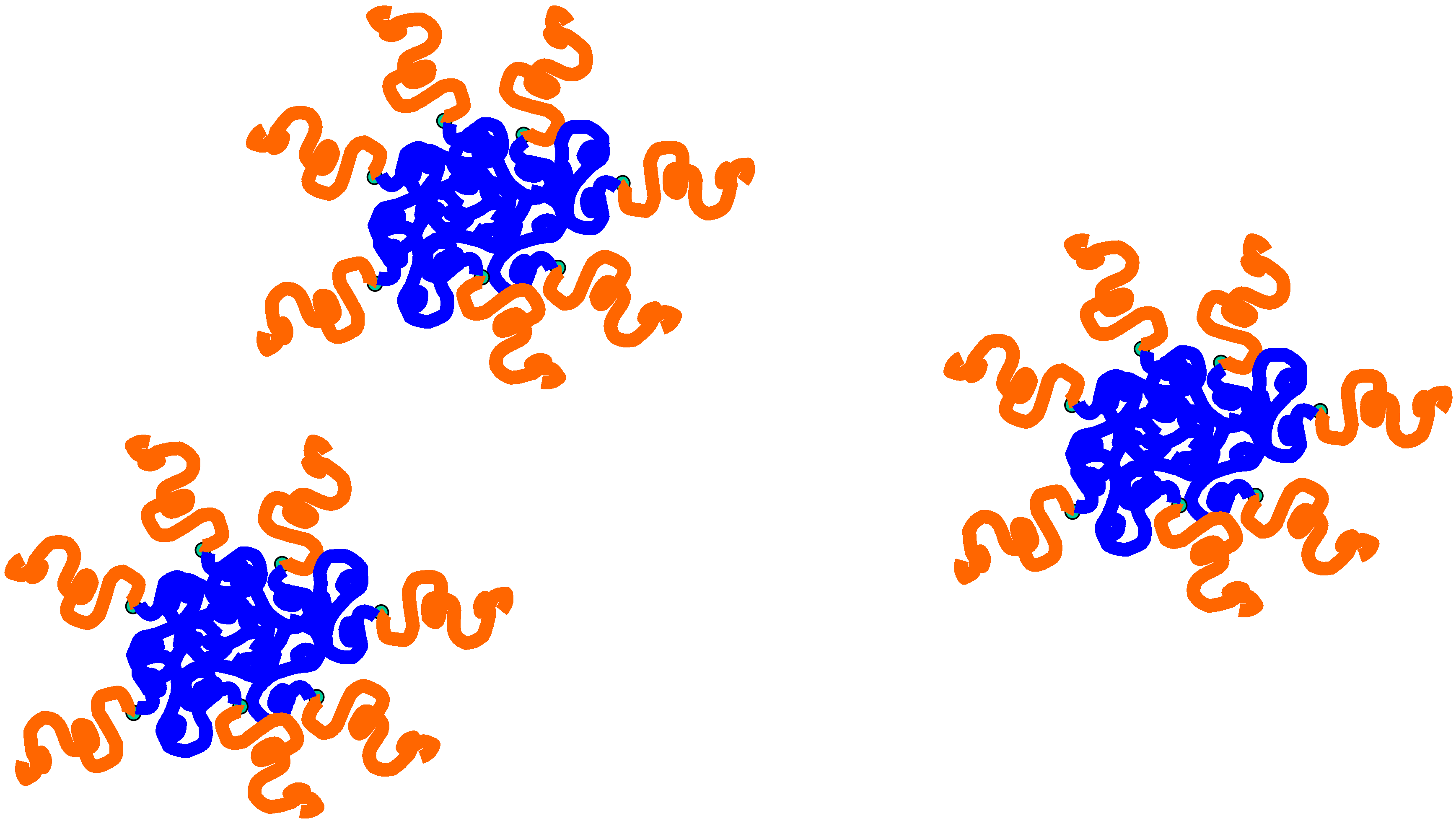


# Diffusion of intact micelles



# Diffusion of intact micelles ($\tau_{diff}$)



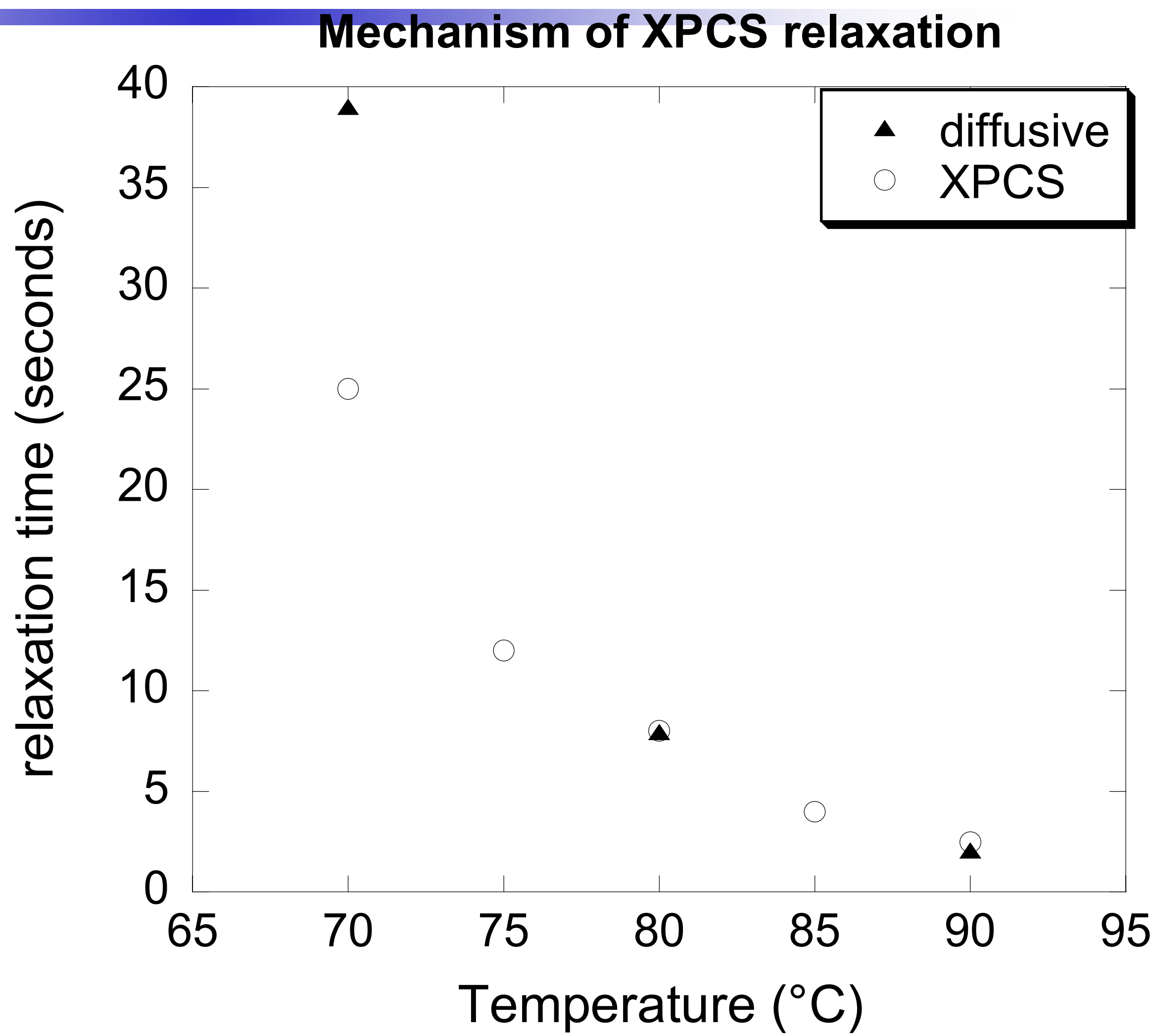
# Intact Micelle diffusion

- Stokes-Einstein diffusion time,

$\tau_{SE}=\pi R_H^3\eta_0(T)/k_B T$ where

$R_H$=hydrodynamic radius of the micelle

$\tau_{diss} >> \tau_{diff}$



# Conclusions

- We have demonstrated the use of XPCS to measure the microscopic dynamics of a block copolymer melt.
- We found that near the ODT, $\tau_{XPCS}$ is greater than $\tau_{rheo}$, in agreement with the Fredrickson-Larson theory.
- Concentration fluctuations relax by diffusion of intact micelles. Stress relaxes by faster process on longer length scales!